CELLULOSE SUPPORTED POLY(AMIDOXIME) Cu/Pd NANOPARTICLES FOR AZA-MICHAEL AND SUZUKI-MIYAURA REACTIONS

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Thesis submitted in fulfillment of the requirements

for the award of the degree of

Master of Science

Faculty of Sciences &Technology

UNIVERSITI MALAYSIA PAHANG

May 2018

ABSTRAK

Kajian ini berkaitan dengan penggunaan mangkin logam heterogen berasaskan selulosa bagi tindak balas Aza-Michael dan Suzuki-Miyaura. Kajian sebelum ini banyak berkisar kepada penggunaan mangkin homogen kerana aktiviti dan keterpilihan pemangkinan yang tinggi. Namun demikian, pemisahan produk dengan mangkin selepas tindak balas serta potensi penggunaan semula mangkin adalah sukar dan terhad. Maka, mangkin heterogen seperti silika, logam oksida, polimer organik, grafin dan bahan komposit berasaskan bio telah digunakan untuk mengatasi masalah ini. Dalam masa yang sama, aspek ekonomi serta persekitaran yang mampan dalam tindakbalas bermangkin gandingan-silang seperti penggunaan bahan kurang berbahaya serta mampan masih belum memenuhi kriteria yang dikehendaki. Oleh itu, penggunaan bahan komposit berasaskan bio adalah salah satu kaedah utama bagi menyokong initiatif ini seterusnya menyelesaikan isu berkenaan kelemahan sistem mangkin homogen tanpa mengurangkan keberkesanan mangkin. Oleh itu, bahan selulosa yang boleh diperolehi dengan mudah dalam kuantiti yang banyak dan murah serta mempunyai kestabilan mekanikal dan kimia yang tinggi, boleh terurai, tidak bertoksik dan mudah dimanipulasi dengan kaedah kimia mempunyai potensi yang tinggi sebagai bahan sokongan mangkin heterogen. Dalam kajian ini, selulosa berasaskan sisa teras jagung yang ditambah logam Pd atau Cu digunakan untuk tindak balas gandingan-silang. Selulosa diekstrak daripada sisa jagung-cob dan diubahsuai menjasi poli(acrylonitrile) dan kemudian poli(amidoxime) chelating ligan, diikuti oleh rawatan dengan $CuSO_4 \cdot 5H_2O$ dan $(NH_4)_2PdCl_4$ untuk menjadi poli berwarna biru (amidoxime) Cu(II) dan poli berwarna coklat(amidoxime) Pd(II) kompleks. Kedua-dua rawatan dengan hidrazin hidrat memberikan nanopartikel tembaga (CuN@PA) dan nanopartikel palladium (PdNs@PA). Pencirian dan perubahan struktur morfologi dikaji dengan menggunakan kaedah spektroskopi seperti FTIR, FESEM-EDX, TEM, XPS, XRD, UV-Vis, TGA dan ICP-AES. CuN@PA (6.8 ± 2 nm) yang berwarna coklat gelap membantu tindak balas Aza-Michael amina alifatik dengan olefin secara efisyen dan selektif bagi membolehkan produk alkyl sepadan sehingga 96% takat suhu bilik. Manakala, PdNs@PA (2.8 ± 6 nm) menunjukkan prestasi pemangkinan yang tinggi bagi tindakbalas gandingan-silang Suzuki- Miyaura aryl halida dengan asid organoboronik untuk memberikan produk biaryl yang sama sehingga 95% dengan jumlah perolehan yang tinggi (TON) 16250 dan kekerapan perolehan (TOF) $5416 h^{-1}$. Dalam kedua-dua tindak balas ini, mangkin heterogen logam nanopartikel menggunakan selulosa sabagai bahan sokongan boleh diguna beberapa kali tindakbalas tanpa menghilangkan keupayaan pemangkinan. Hasil kajian ini membuktikan bahawa bahan selulosa berasaskan sisa teras jagung boleh digunakan sebagai bahan sokongan mangkin yang sesuai bagi tindakbalas Suzuki- Miyaura dan Aza-Michael seterusnya menyokong pengunaan teknologi hijau dalam kelestarian pembangunan teknologi terkini.

ABSTRACT

This research is mainly focused on the utility of cellulose supported heterogenous metal catalyst for Aza-Michael and Suzuki-Miyaura reactions. Such reactions are generally conducted by homogeneous catalyst, but the untidy reactions, difficulties in separation of product from reaction mixture, removal and reuse of homogenous catalyst lies as the limitations. Thus, heterogeneous catalysts with different types supports, such as silica gel, metal oxide, organic polymers, graphene and various hybrid inorganic materials have been employed to overcome these issues. Nowadays researchers have developed many economic and environmental sustainable catalytic protocols to develop the process of cross-coupling reactions in green perspective but till now it is difficult to meet the criteria of being safely reusable, non-toxic, chemically sustainable, and organic synthesis catalyst. The development of bio-based materials and composites could be considered as a promising solution of these demerits both in terms of environmental and performances aspects. From this point of view, natural biopolymers (cellulose) could be considered as more acceptable solid support material because it has some promising qualities as widely abundance in nature, bio-degradability, high chemical and mechanical stability, easily chemically modified, bio-renewability**,** non-toxicity, cheap and environmental friendly. Therefore, cellulose can act as a suitable candidate as solid support for heterogeneous catalytic system. On focusing to this target firstly, cellulose was extracted from waste corn-cob and chemically modified by poly(acrylonitrile). Then resulting polymeric functional group was converted into suitable poly(amidoxime) chelating ligand, followed by treatment with metal (Cu/Pd) salt to afford the related cellulose supported heterogeneous poly(amidoxime) metal complexes. Both complexes were treated with hydrazine hydrate to produce nano-sized cellulose supported poly(amidoxime) copper nanoparticles (**CuN@PA**) and palladium nanoparticles (**PdNs@PA**). The characterization and morphological changes were confined by using several spectroscopic techniques such as fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDX), x-ray photoelectron spectroscopy (XPS), x-ray powder diffraction (XRD), ultraviolet-visible spectrophotometry (UV-vis), thermogravimetric analysis (TGA) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses. The dark brown coloured **CuN@PA** (size- 6.8 ± 2 nm) was efficiently catalyzed Aza-Michael reaction of aliphatic amines with different olefins to afford the corresponding alkylated products up to 96% at room temperature. Whereas **PdNs@PA** (size- 2.8 ± 6 nm) showed high catalytic performance towards Suzuki-Miyaura cross-coupling reaction of aryl halides with organoboronic acids to give the corresponding biaryl products up to 95% yield with high turnover number (TON) 16250 and turnover frequency (TOF) 5416 h^{-1}. In both reactions, the cellulose supported nanoparticles were easy to recover and reused several times without a significant loss of their activity. Thus, a bio-based and effective cellulose supported heterogeneous metal catalyst was prepared from completely waste material (corn-cob) and applied efficiently to two popular reaction, Aza-Michael and Suzuki-Miyaura reactions. This cellulose supported metal catalyst would be a great achievement not only in the green industrial aspect but also a variety of natural products can be synthesized by using heterogeneous catalyzed key step reaction.